

## REMARKS/ARGUMENTS

Claims 44-49 and 104-148 are active in this application.

Claims 47-49, 105-109, 111-115, 117, 118, 120-124, 127-130, 132, 133, 137-142 and 145-148 were withdrawn from consideration by the Examiner.

The amendment to Claim 44 is amended to clarify that the polymer does not exhibit an LCST itself rather there are units contained in the polymer which exhibit the LCST and further that the polymer comprises an oligomer and copolymer of water-soluble units. This amendment is supported throughout the specification, e.g., page 4, lines 16-25; page 5, lines 6-15; and page 8, lines 4-6.

No new matter is believed to be added. Favorable reconsideration is requested.

The rejections of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136 and 143-144 under 35 U.S.C. § 102(b) over U.S. 4,737,265 (“Merchant”); U.S. 4,839,167 (“Yamamoto”); or U.S. 5,338,352 (“Breneman”); JP61245835 (“Ezaki”); U.S. 4,274,977 (“Koerner”); U.S. 4,559,226 (“Fogel”); EP 1055694 (“Yabuta”), EP 583814 or EP629649 (collectively “The Maroy publications”) are respectfully traversed.

These rejections are not tenable because none of the publications describe the claimed method of lowering the surface tension or the interface tension of water by adding a polymer to water in an amount sufficient to lower the surface tension or the interface tension of water as claimed. More specifically, the cited references describe different polymers from those employed in the claims, i.e., (1) the polymers in the cited publications have a cloud point (exhibit an LCST); and/or (2) the polymers in the publications have LCST units having a demixing temperature (cloud point) exceeding 40°C; and/or (3) the polymers in the publications do not contain an oligomer or copolymer of water-soluble units. Further discussion on these points follow.

Merchant

Merchant describes a maleic anhydride grafted to an alkyl phenol formaldehyde resin in col. 6, lines 41-49. This compound contains a single maleic anhydride unit. However, as defined in the pending claims, the polymer in the claims includes an oligomer or copolymer of LCST units with the water-soluble units.

Merchant also describes p-nonyl phenyl formaldehyde resin having 10 moles of ethylene oxide in the Examples section of the specification (see col. 10, lines 42-45 and col. 11, lines 29-30). This is also not the same as the polymer in the present claims because the 10 moles of ethylene oxide contained in the polymers are not LCST units as supported by the attached publication of Malcom and Rowlinson. Specifically, attention is directed to the phase diagram of Figure 6 on page 926. This Figure shows phase diagrams for polyethylene oxide (indicated in squares and crosses) in which above the curve there exists two phases, below the curve there exists one phase, and the lowest point of the curve defines the LCST. Therefore, this Figure shows that as the molecular weight of the polyethylene oxide gets smaller, the two phase domain also gets smaller. Also illustrated is that for a POE of 3000, the two phase domain is indicated as the oval in the Figure. Taken together then, 10 units of polyethylene oxide as is the case in Merchant would only exhibit 1 phase, i.e., no LCST.

Withdrawal of the rejection in view of Merchant is requested.

Breneman

Breneman describes an organomodified silicone emulsifier (col. 2, line 13) in which heating and agitation are required to form an oil-in-water emulsion (col. 3, lines 34-35).

Breneman also describes a polyether modified polysiloxane, which is a copolymer of hydrophilic and hydrophobic monomers. These polymers do not contain water-soluble units and LCST units as in the claimed dispersion.

Yamamoto

Yamamoto describes hair care products with an emulsion containing a hair fixative polymer which is water soluble (col. 2, line 10-23 and col. 3, lines 45-46) and can be one of several polymers listed in col. 3, lines 51-63 none of which are a polymer of water-soluble units and LCST units in the claimed dispersion. For example, in col. 3, line 51-53 of Yamamoto, a polyvinylpyrrolidone compound such as copolymer of vinylpyrrolidone and vinyl acetate is described. Both vinylpyrrolidone and vinyl acetate monomers form water-soluble units (see page 9, line 29 through page 11, line 13 of the present application) but Yamamoto does not describe a polymer with LCST units.

Ezaki

Ezaki describes a nonionic surfactant with a specific cloud point. Ezaki does not describe any polymer as required in the present claims, having water-soluble and LCST units such that the polymer does not exhibit an LCST and comprises an oligomer or copolymer of water-soluble units.

Koerner

Koerner describes an alkyl polyether at the top of col. 8, which polymer has a cloud point, i.e., the polymer exhibits an LCST, at a specific temperature and concentration (col. 8, lines 1-6). This polymer, however, is different from the polymer defined in the claims where the polymer does not exhibit an LCST.

Moreover, the polymers described elsewhere in Koerner, e.g., columns 5 and 6, also have a cloud point (see col. 6, lines 24-29) and thus are not the same as the polymer defined in the claimed dispersion.

Withdrawal of the rejection in view of Koerner is requested.

Fogel

Fogel in col. 2 describes an alkoylate ester of a specific formula where  $R_2$  can be either (a) or (b) and x is from 1 to 10 (see lines 53-62). Polyoxypropylene groups, e.g., when x is 10, have a molecular weight of 580 g/mol and as shown on the attached technical sheet have a demixing temperature, i.e., cloud point, at a 1% concentration of 65°C (see P600E) (Dow Corning Technical Sheet: polypropylene glycol). Furthermore, where x is less than 10, the demixing temperature, i.e., cloud point, is much greater than 65°C (see, e.g., P400E). Therefore, the polymers in Fogel are unquestionably different from the polymer defined in the claims, i.e., having LCST units with a demixing temperature of 5 to 40°C at a concentration of 1%.

Withdrawal of the rejection in view of Fogel is requested.

Yabuta

Yabuta describes a block copolymer of ethylene glycol and propylene glycol, which polymer has a cloud point, i.e., the polymer exhibits an LCST, in the 30 to 90°C range (see [0096] and [0097] on page 11). This polymer, however, is different from the polymer defined in the claims where the polymer does not exhibit an LCST. Withdrawal of the rejection based on Yabuta is requested.

Maroy publications

The Maroy publications are acknowledged and discussed on page 1, lines 24-25 and page 2, lines 10-14 of the present specification, noting that documents [4] and [5] are the Maroy publications. The Maroy publications describe a polymer with water-soluble groups and LCST groups (page 2, lines 26-30 of EP '814). Maroy also describes that the groups with

LCST can be copolymerized with the water-soluble groups or grafted onto a hydrosoluble skeleton (page 2, lines 34-44 of EP '814).

Maroy does not describe a polymer containing LCST units having a demixing temperature of 5 to 40°C at 1% by mass in water in the claimed method. In fact, the LCST units described in the Maroy publications do NOT have, in water, a demixing temperature of from 5 to 40°C at 1% by mass in water. Specifically, on page 2, lines 53-56 and page 3, lines 2-3 of EP '814 and col. 2, line 54 to col. 3, line 4, Maroy describes that the LCST units selected from polyethyleneglycol (POE), polyoxypropylene (POP) or polyoxide of ethylene and propylene (POEP). Furthermore, Examples 1.1, 1.2, 1.3, and 1.4 of EP '814 (Maroy) on pages 3-4, all describe polymers with POE5 as the LCST units, which is polyethyleneglycol with a molecular weight of 5000 g/mol. However, these polymers have a demixing temperature above 100°C at a concentration of 1 % by mass (see page 5, line 41, page 6, lines 37-39, and page 6, lines 57-59 of EP '814). Therefore, these polymers cannot be the same as the polymer defined in the claimed dispersion (having a demixing temperature of 5 to 40°C at 1% by mass in water).

In Example 2.3 (page 7) of EP '814 (Maroy), the polymer contains POP of a molecular weight of 600 as the LCST unit. However, unlike the polymer in the claimed dispersion, this polymer of Maroy has a demixing temperature of 48°C at a concentration of 1 % by mass. In Example 2.5 (pages 7-8) of EP '814 (Maroy), the polymer contains a POEP polymer with a molecular weight of approximately 1100. However, unlike the polymer in the claims, this polymer has a demixing temperature above 60°C (see Figure 3 of EP '814).

In the Examples of EP '649, Maroy describes the same example as 1.2 from EP '814 (see the reference to French application 9210224, which is the priority application of EP '814 in col. 6, line 40 and lines 54-56) and Examples 4 and 5 which include POE with a molecular weight of about 5000. For the same reasons as discussed above concerning EP '814, these

specifically described polymers have a demixing temperature above 60°C and are therefore NOT the same as the polymer set forth in the claims.

Withdrawal of the rejections based on the Maroy publications is requested.

Applicants request that the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 under the doctrine of obviousness type double patenting in view of claims 25-67 of co-pending application no. 10/069,981 be held in abeyance since the alleged conflicting claims have not yet been patented. Further, Applicants note the following from MPEP § 822.01:

The "provisional" double patenting rejection should continue to be made by the examiner in each application as long as there are conflicting claims in more than one application unless that "provisional" double patenting rejection is the only rejection remaining in one of the applications. If the "provisional" double patenting rejection in one application is the only rejection remaining in that application, the examiner should then withdraw that rejection and permit the application to issue as a patent, thereby converting the "provisional" double patenting rejection in the other application(s) into a double patenting rejection at the time the one application issues as a patent.

The rejection of Claim 119 under 35 U.S.C. § 112, second paragraph is obviated by the amendment submitted herein.

Accordingly, withdrawal of the rejection is requested.

Application No. 10/069,983

Preliminary Amendment filed with a Request for Continued Examination

Applicants also request allowance of this application.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



---

Richard L. Treanor, Ph.D.  
Attorney of Record  
Registration No. 36,379

Daniel J. Pereira, Ph.D.  
Registration No. 45,518

Customer Number  
**22850**

Tel: (703) 413-3000  
Fax: (703) 413 -2220

# THE THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL, POLYPROPYLENE GLYCOL AND DIOXANE

BY G. N. MALCOLM \* AND J. S. ROWLINSON  
Dept. of Chemistry, University of Manchester

*Received 7th March, 1957*

Measurements are reported of the vapour pressures, the heats of mixing, the densities and the phase relationships of solutions of polyethylene glycol and polypropylene glycol in water. The free energies, heats and entropies of dilution, the volume changes on mixing and the excess partial volumes have been derived. The results show significant differences from those for other polar polymer solutions. A comparison is made with the results for aqueous solutions of dioxane which is the cyclic dimer of the repeating unit in polyethylene glycol. Some new measurements of the vapour pressures of dioxane + water solutions at temperatures between 100° C and 156° C and of the heat of mixing at 25° C, are reported in an appendix.

Few precise measurements have yet been made of the thermodynamic properties of polymer solutions which contain polar molecules. This paper reports the results of a detailed investigation of the properties of the solutions of polyethylene glycol and polypropylene glycol in water. These solutions provide examples of polymer solutions in which association and clustering of solvent molecules may occur and in which orientation-dependent interactions are present between solvent and polymer. Polyethylene glycol and polypropylene glycol were chosen because they are the simplest available polyethers. Several other polyethers are in course of preparation for future study.

## EXPERIMENTAL

**MATERIALS.**—Samples of polyethylene and polypropylene glycols were kindly supplied by Oxirane Ltd. of Manchester. The number average molecular weights were given as 5000, 3000, 1500 and 300 for the polyethylene glycols and 750 and 400 for the polypropylene glycols. The solid samples were purified before use by reprecipitation with hexane from hot carbon tetrachloride solution. All the samples were carefully dried under high vacuum.

**VAPOUR PRESSURE MEASUREMENTS.**—The difference between the vapour pressure of the solution and that of pure water at the same temperature was measured with a mercury manometer in an apparatus similar to that used by Taylor and Rowlinson.<sup>1</sup> Times of up to 36 h were necessary for the pressure differences to become steady. The constancy of the thermostat was  $\pm 0.01$  deg. at 25° C and  $\pm 0.04$  deg. at 65° C. The thermometers were calibrated against thermometers standardized by the N.P.L. A correction for the vapour space was applied when calculating the concentrations. Measurements of the vapour pressure of water made with this apparatus agreed well with those recommended by Dorsey.<sup>2</sup>

**HEAT OF MIXING MEASUREMENTS.**—These were performed in an isothermal naphthalene calorimeter, which was a much enlarged version of the instrument described by Beynon and Humphries.<sup>3</sup> The central tube of the calorimeter was made 2 in. wide and 20 in. long. The lower 6 in. of this tube were separated from the rest by an evacuated B 55 ground glass stopper. A thin central tube through the stopper allowed two nylon threads to pass to the mixing vessel inside the reaction chamber. Two additional heat reflecting

\* present address : Otago University, Dunedin, New Zealand.



shields were added to those described by Beynon and Humphries. One of these was an aluminium foil sheet placed on the bottom face of the glass stopper. The other was a polished brass disc which was fixed immediately above the stopper and was heated electrically to maintain it at the temperature of the thermostat.

The mixing vessel, shown in fig. 1, was a glass sphere of 4 cm diameter divided into two compartments by an inner tube and a layer of mercury. When solid polymer material was used it was placed in the outer compartment, O, melted, solidified and weighed.

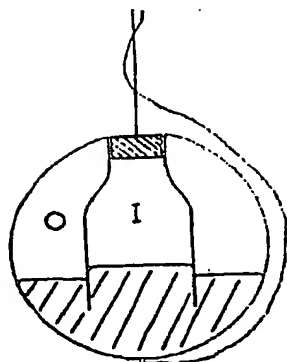


FIG. 1.—Mixing vessel.

Mercury was added completely to fill the outer compartment, and the requisite amount of water was then added to the inner compartment, I, from a weight burette. Liquid polymer material was placed on top of mercury in the outer compartment by means of a hypodermic syringe, and the water was then added as before. The vessel was closed by means of a tightly fitting rubber bung so that no vapour space remained. The bung was initially inserted well inside the vessel so that the slight expansion of the contents which occurred on heating up to 80° C was taken up by allowing the bung to be driven upwards until it pressed against a strong wire fastened round the vessel. Mixing and stirring were achieved by repeatedly tipping the vessel upside down by means of the nylon threads. The movement of the mercury served both to stir the solution and also to conduct the heat of mixing rapidly to the outer wall of the vessel. From there the heat was conducted by a silicone oil to the wall of the naphthalene chamber. (The level of the oil in the

reaction chamber was always below the top of the naphthalene chamber.) The movement of the mercury in the capillary was measured with a cathetometer.

The sensitivity of the calorimeter was  $1.544 \pm 0.007$  cm/cal (1 cal = 4.1840 joules). This figure gave a value of 0.00429 cm<sup>3</sup>/cal for the volume change of naphthalene on fusion, which agreed well with the values 0.00427 and 0.00433 cm<sup>3</sup>/cal recorded by Beynon and Humphries for their work and that of Coffin.<sup>4</sup> The apparatus was placed in a bath which could be maintained at constant temperature to within  $\pm 0.001^\circ$  C for periods of several hours. During an experiment variations in the rate of background drift of the mercury in the capillary tube were not more than 0.001 cm/sec. In each experiment amounts of the order of 1 to 6 g of each substance were used, and were chosen so that between 20 and 40 cal were evolved on mixing (except in the regions of extreme dilution or concentration). The time of a complete mixing experiment was usually 90 min, so that the maximum error which could be caused by change in the rate of background drift was 0.6 %.

**DENSITY MEASUREMENTS.**—The densities of the solutions were measured in a bi-capillary pyknometer, which was filled by means of a hypodermic syringe. The pyknometer was calibrated at each temperature with distilled water.

**PHASE SEPARATION MEASUREMENTS.**—These were carried out by heating the solutions in Pyrex tubes. Each tube contained a short length of glass rod to aid stirring, and after filling with solution, was frozen, evacuated and sealed off. Heating up to 250° C was carried out in an oil bath. The temperature of incipient phase separation was first noted as the bath was slowly warmed (or cooled), and was compared with the temperature at which the solution first became clear again. Readings up to 150° C could be reproduced to within  $\pm 0.1^\circ$  C, those up to 200° C to  $\pm 1^\circ$  C and above 200° C to  $\pm 2^\circ$  C.

## RESULTS

### VAPOUR PRESSURE MEASUREMENTS

The vapour pressures and the solvent activities as functions of the polymer weight fraction are shown in tables 1 and 2.

The experimental error in the measured pressure differences is thought to be within  $\pm 1\%$ , and the error in the weight fractions is less than this amount. The vapour pressure values for water used in the calculation of the activities are those recommended by Dorsey.<sup>2</sup> Correction for the imperfection of the vapour was made using the equation of state of Keyes, Smith and Gerry.<sup>2</sup>

For all four solutions the vapour pressure isotherms are everywhere convex towards the vapour pressure axis. In this respect they differ from the isotherms for the nitro-cellulose + ketone systems<sup>3</sup> and the agar-agar + water system,<sup>6</sup> which have sigmoid

shapes. The vapour pressure curves were not dependent on whether the water concentration was being increased or decreased; that is, there was no hysteresis.

TABLE 1.—THE VAPOUR PRESSURES IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL

temp. °C	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )
MOLECULAR WEIGHT 5000						
65.00	0.990	35.71	0.191	0.835	150.73	0.805
	0.970	78.92	0.422	0.764	160.58	0.857
	0.951	102.31	0.547	0.735	165.62	0.884
	0.949	103.24	0.552	0.662	171.30	0.914
	0.902	132.48	0.708	0.496	182.79	0.974
	0.900	133.11	0.711	0.000	187.54	1.000
	0.839	150.33	0.803			
60.00	0.950	81.50	0.547	0.735	130.91	0.877
	0.902	104.22	0.699	0.000	149.38	1.000
	0.835	118.70	0.796			
MOLECULAR WEIGHT 3000						
65.00	0.990	34.36	0.184	0.846	145.01	0.774
	0.970	75.03	0.402	0.765	158.70	0.847
	0.950	99.26	0.531	0.704	166.34	0.888
	0.904	127.01	0.679	0.499	181.72	0.969
	0.897	130.46	0.697	0.000	187.54	1.000
55.00	0.970	47.10	0.400	0.702	102.62	0.871
	0.950	61.74	0.524	0.499	113.76	0.964
	0.844	89.45	0.759	0.000	118.04	1.000
MOLECULAR WEIGHT 300						
65.00	0.988	24.97	0.134	0.662	156.12	0.833
	0.951	63.95	0.342	0.489	173.54	0.926
	0.900	97.13	0.520	0.299	181.89	0.970
	0.801	132.31	0.707	0.000	187.54	1.000
50.00	0.988	12.12	0.132	0.660	75.58	0.818
	0.950	30.31	0.329	0.488	84.77	0.917
	0.899	46.07	0.499	0.298	89.39	0.966
	0.800	63.11	0.683	0.000	92.51	1.000
30.00	0.988	3.95	0.124	0.659	25.10	0.789
	0.950	9.81	0.309	0.488	28.65	0.900
	0.899	14.88	0.468	0.298	30.41	0.956
	0.800	20.61	0.648	0.000	31.82	1.000

TABLE 2.—THE VAPOUR PRESSURE IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYPROPYLENE GLYCOL 400

temp. °C	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )
50.00	0.990	19.90	0.216	0.701	90.99	0.984
	0.952	59.13	0.640	0.591	91.68	0.991
	0.902	78.94	0.854	0.000	92.51	1.000
	0.801	89.05	0.963			
30.00	0.990	6.62	0.208	0.700	31.12	0.978
	0.950	19.88	0.625	0.590	31.36	0.985
	0.901	26.89	0.845	0.000	31.82	1.000
	0.800	30.40	0.955			

## CALOMETRIC MEASUREMENTS

The heat of mixing results are recorded in table 3.

TABLE 3.—THE HEATS OF MIXING AT 80.3° C FOR AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL IN cal/g OF MIXTURE AS A FUNCTION OF THE WEIGHT FRACTION OF POLYMER ( $W_2$ )

$W_2$	$-\Delta H$ cal/g	$W_2$	$-\Delta H$ cal/g
MOLECULAR WEIGHT 5000			
0.206	4.79	0.755	4.89
0.336	7.03	0.825	3.25
0.480	8.20	0.887	1.39
0.548	7.91	0.953	0.30
0.675	6.18		
MOLECULAR WEIGHT 3000			
0.102	2.32	0.780	4.66
0.303	6.59	0.847	2.87
0.517	8.14	0.904	1.33
0.719	5.92		
MOLECULAR WEIGHT 300			
0.287	6.29	0.820	5.26
0.475	8.05	0.897	3.10
0.630	7.44	0.948	1.42
0.719	6.59		

The probable error in the heat of mixing per gram of mixture is  $\pm 2\%$ . A comparison between these results and those for the dioxane + water system (see appendix) is made in fig. 2.

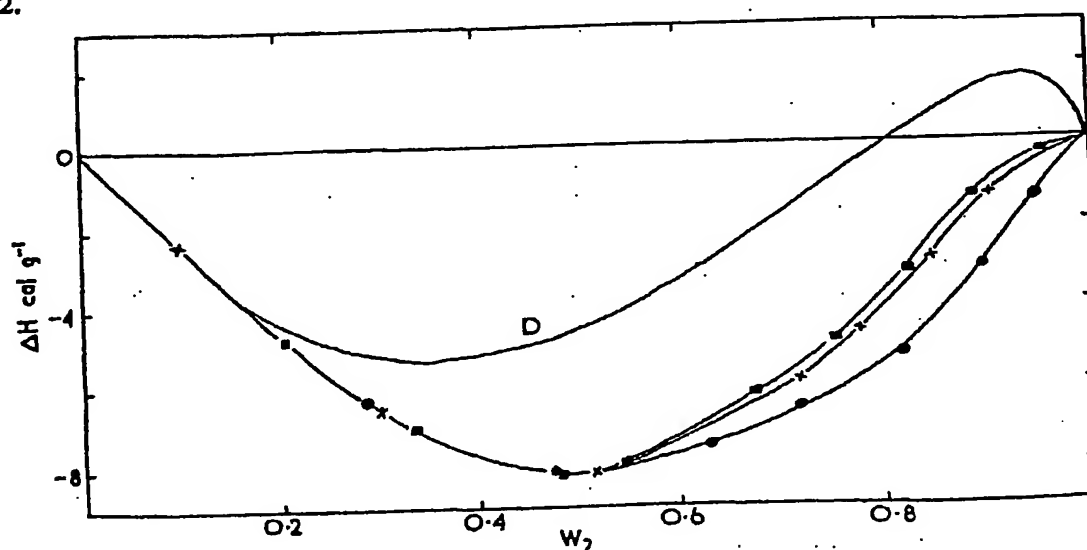


FIG. 2.—Heats of mixing at 80.3° C of polyethylene glycol and water plotted against weight fraction of polymer. Squares, mol. wt. 5000; crosses, mol. wt. 3000; circles, mol. wt. 300. Curve D, dioxane and water (20° C).

## THERMODYNAMIC DILUTION FUNCTIONS

The results in tables 1-3 were used to calculate free energies and heats of dilution for the four solutions. For the three polyethylene glycol solutions the free energies of dilution at 65° C and the heats of dilution at 80.3° C were combined to give approximate values of the entropies of dilution. (The heats of dilution calculated at several temperatures from the vapour pressure measurements indicate that the temperature coefficient of the heat of dilution is small and positive.) For the polypropylene glycol solutions the heats of dilution were calculated from the vapour pressure measurements, and are the mean

FIG. 3.—Thermodynamic dilution functions plotted against weight fraction of polymer or dioxane (see text). A and B, polyethylene glycols 5000 and 300; C, polypropylene glycol 400; D, dioxane.

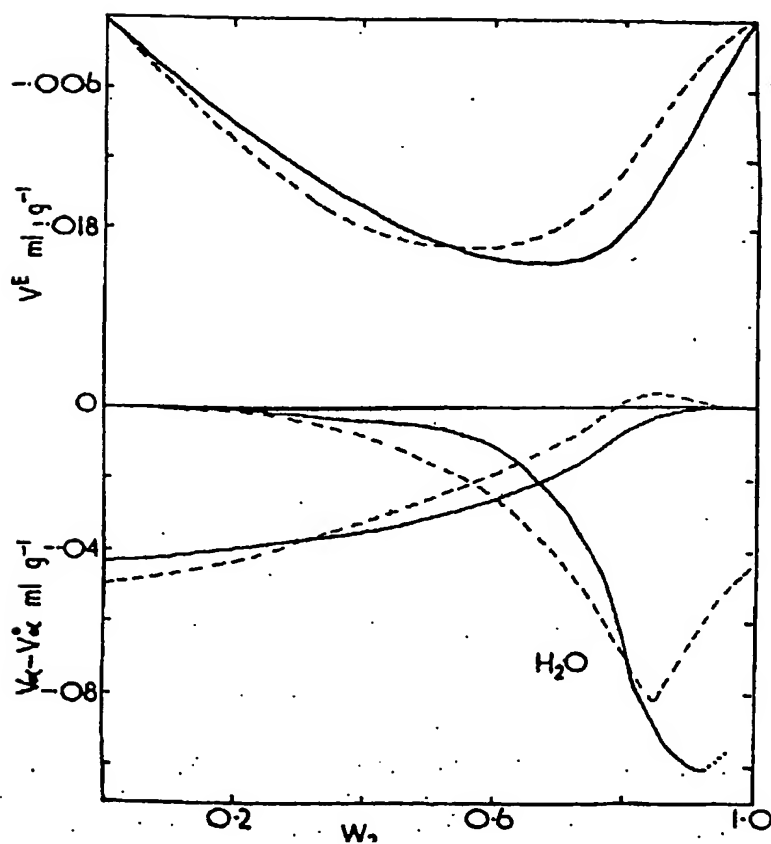
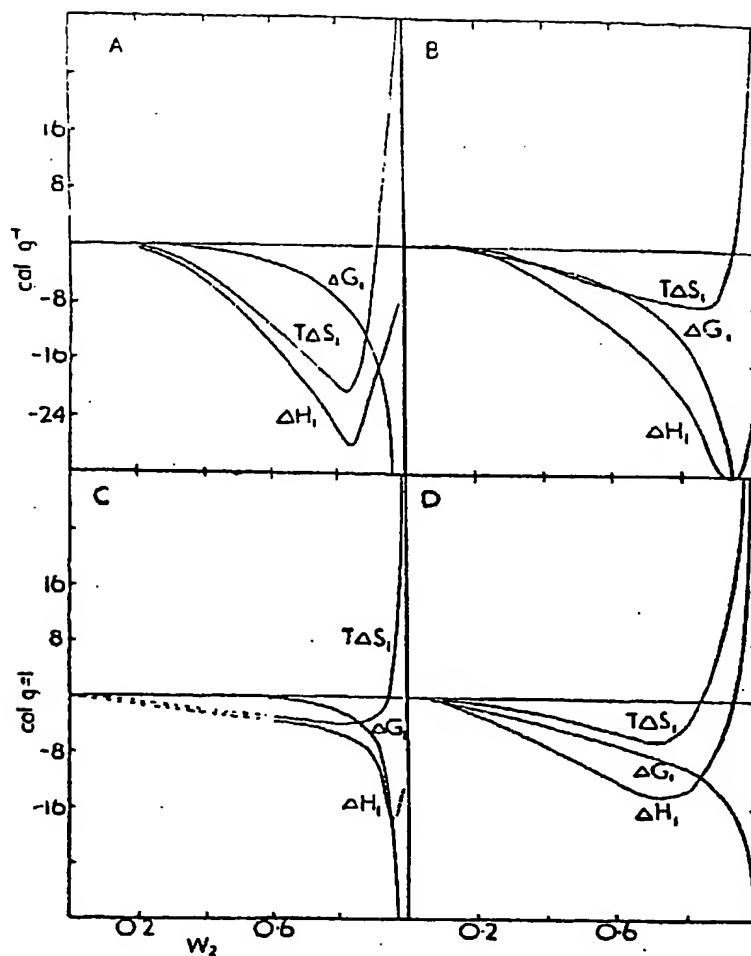


FIG. 4.—Excess volumes and excess partial volumes as functions of weight fraction of polymer or dioxane. Full lines, polyethylene glycol 5000 at 65° C; broken lines, dioxane at 25° C.

values between 30° C and 50° C. The smoothed values of the three dilution functions are plotted in fig. 3. Fig. 3(D) shows the dilution functions for the dioxane + water system calculated from vapour pressures at 25° C and heats of mixing at 20° C (see appendix). The curves for the solution of polyethylene glycol 3000 are very similar to those for the sample of molecular weight 5000, and are not plotted in the figure.

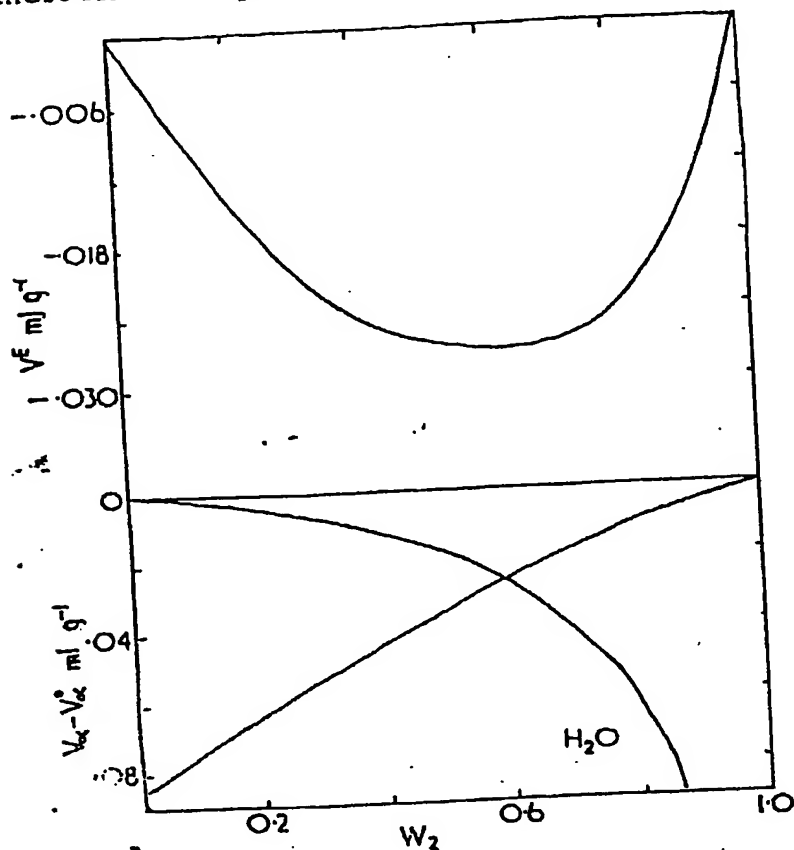
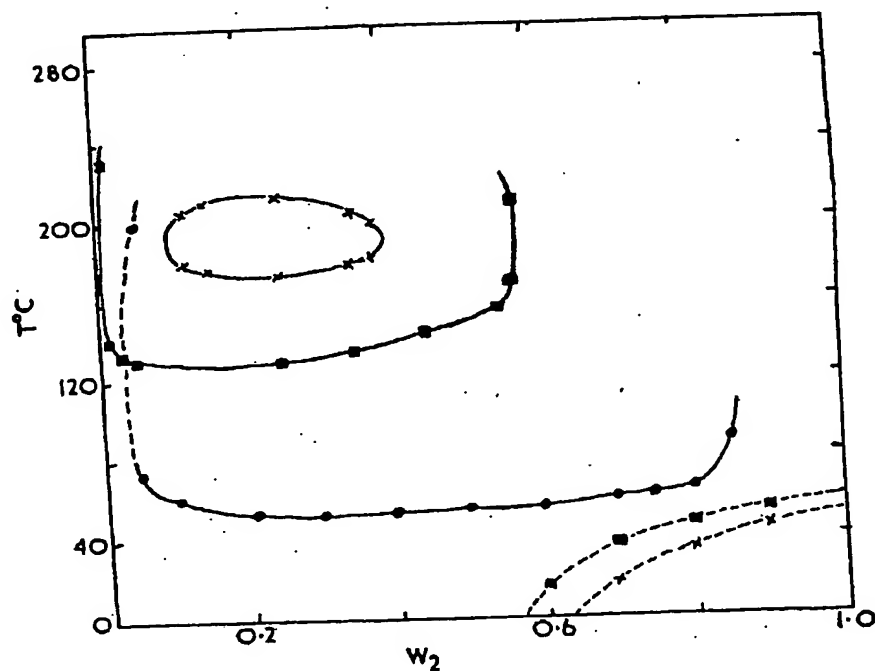


FIG. 5.—Excess volumes and excess partial volumes in solutions of polypropylene glycol 400 at 50° C as functions of the weight fraction of polymer.

FIG. 6.—Phase diagram for aqueous solutions of polyethylene and polypropylene glycols. Squares and crosses, polyethylene glycols 5000 and 3000; circles, polypropylene glycol 400. Lower right-hand curves, solid-liquid boundaries.



#### VOLUME CHANGES ON MIXING

The densities of the solutions of the three polyethylene glycols plotted against composition fell on the same smooth curve. The results were used to calculate the excess volume of the mixture and the excess partial volumes of the components. These functions

are plotted in fig. 4, together with the corresponding results for the dioxane + water solution (see appendix). The results for the polypropylene glycol solutions are shown in fig. 5.

#### PHASE RELATIONSHIPS

The phase diagrams which were obtained are shown in fig. 6. No phase separation was observed in the solutions of polyethylene glycol 300 or dioxane.

### DISCUSSION

Analysis of the results for the solution of polyethylene glycol 5000 in terms of the free energy equation

$$\Delta G_1 = RT\{\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2\} \quad (1)$$

gives values of the parameter  $\chi$  which increase uniformly with volume fraction of polymer ( $\phi_2$ ) from 0.4 at  $\phi_2 = 0.25$  to 0.75 at  $\phi_2 = 0.66$ , and then increase more rapidly to 1.24 at  $\phi_2 = 0.9$ .

For the nitrocellulose + ketone systems and the agar-agar + water solution the values of  $\chi$  decreased with increase in  $\phi_2$  and were negative at high concentrations of polymer. This difference in behaviour is further illustrated by the fact that the vapour pressure isotherms of the solutions studied here are not sigmoid in shape like those of the nitrocellulose and agar-agar solutions.

Examination of the thermodynamic dilution functions is interesting in this connection. For the solution of polyethylene glycol 5000 the excess of the entropy and heat of dilution over the values predicted by the equations,

$$\Delta S_1 = -R\{\ln(1 - \phi_2) + \phi_2\}, \quad (2)$$

and

$$\Delta H_1 = 0, \quad (3)$$

have been calculated, and are plotted with the corresponding free energy quantity in fig. 7.

(For convenience in the following discussion the differences between the observed dilution functions and those given by eqn. (2) and (3) are called "excess" dilution functions.) From fig. 7 it is apparent that the "excess" entropy of dilution determines the sign of the "excess" free energy, and makes it positive despite the negative heat of dilution. Consequently the values of the parameter  $\chi$  in eqn. (1) are positive. In the agar-agar + water system at high polymer concentrations the negative "excess" entropy of dilution is numerically less than the exothermic heat of dilution, so that the "excess" free energy in this region is negative and gives negative values of  $\chi$ . No entropy or heat of dilution values are yet available for the nitrocellulose solutions.

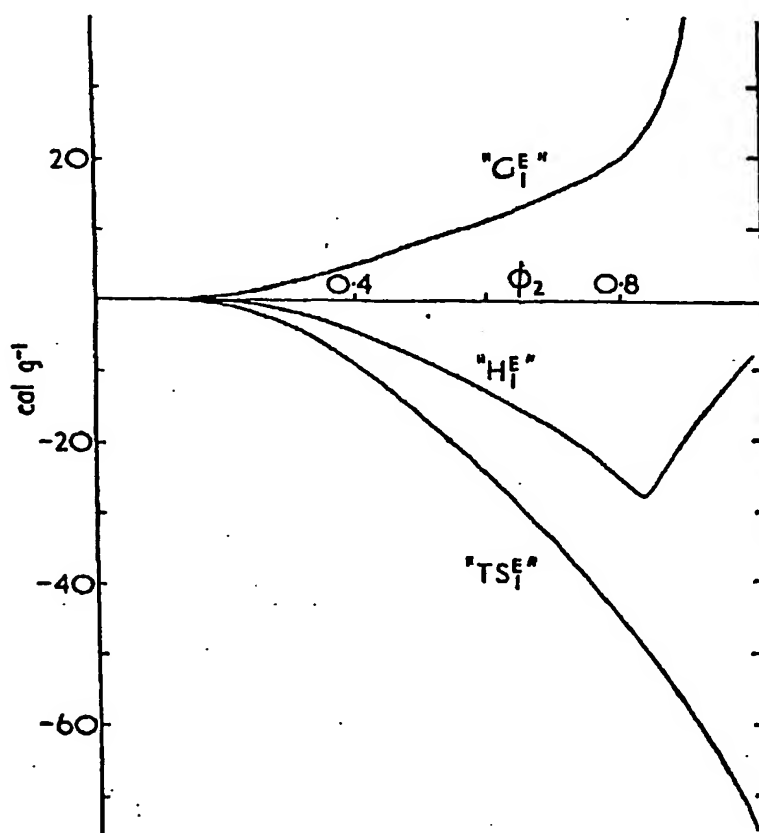


FIG. 7.—"Excess" thermodynamic dilution functions for the solution of polyethylene glycol 5000 (see text).  $G_1^E$  and  $TS_1^E$  at 65° C,  $H_1^E$  at 80.3° C.

Fig. 7 reveals that the much greater increase in the value of  $X$  which was found in the region of high polymer concentration results from the sudden change in slope of the heat of dilution curve, which passes through a minimum. Similar behaviour in the heat of dilution is found in the dioxane + water system (fig. 3D) and in the ethanol + water system.<sup>7</sup> The vapour pressure results for the solution of polypropylene glycol suggest that the same behaviour is present there (fig. 3C).

The appearance of lower consolute temperatures in the solutions of the higher polyethylene glycols is another indication that negative entropies are determining the solution behaviour. Lower consolute temperatures have seldom been observed in polymer solutions.

The heat of mixing results in fig. 2 reveal marked differences in the behaviour of polymer molecules which seemingly differ only in chain length. It might reasonably have been anticipated that the dioxane curve would lie below that for the lowest polymer, since it contains only two ethylene oxide units. But the observed heats of mixing are in the same sequence as the proportions by weight of hydroxyl end groups in the various molecules, so that it seems probable that the end groups are responsible for the differences in behaviour. This hypothesis is supported by the results of some simple test-tube experiments with two related substances, ethylene glycol dimethyl ether and ethylene glycol monomethyl ether. The heat of mixing for the first of these substances, which contains no hydroxyl group, was positive for low water concentrations and became negative when the weight fraction of water reached 0.15. Addition of small quantities of water to the monomethyl ether resulted in a negative heat of mixing of a similar magnitude to that observed in the concentrated solutions of polyethylene glycol 300.

We wish to thank Prof. Gee for suggesting this work and for discussion of the results. We are grateful to Dr. A. J. Lowe of Oxirane for information concerning the polymers. One of us (G. N. M.) acknowledges with thanks the award of an Overseas Scholarship from New Zealand by the Royal Commission for the Exhibition of 1851.

## APPENDIX

### THE SYSTEM DIOXANE + WATER

(with A. Davis)

The vapour pressures of aqueous solutions of dioxane have been measured by Hovorka, Schaeffer and Dreisbach<sup>8</sup> (0–80° C), by Vierk<sup>9</sup> (25° C) and by Bacarella, Finch and Grunwald<sup>10</sup> (25° C). Vierk has also measured the heat of mixing at 20° C and Stallard and Amis<sup>11</sup> the heat capacity at 40° C. The densities have been measured, amongst others, by Hovorka, Schaeffer and Dreisbach and by Griffiths,<sup>12</sup> both of whom calculate the partial molar volumes at 25° C. These measurements show clearly that at room temperature this system has a positive excess Gibbs free energy, a negative excess enthalpy and a negative excess volume in mixtures weak in dioxane. This is the behaviour of solutions which show lower consolute points. We have therefore analysed these measurements further and have supplemented them with measurements of the vapour pressure up to 156° C and a search for such a consolute point up to 240° C.

**PREVIOUS MEASUREMENTS.**—We have disregarded the vapour pressures of Hovorka, Schaeffer and Dreisbach as their partial pressures at 25° C do not satisfy the Gibbs-Duhem equation and their total pressures are not in agreement with those of Bacarella, Finch and Grunwald. The partial pressures and activities of Vierk are satisfactory and lead to the excess free energy shown in fig. 8. The measurements of Bacarella, Finch and Grunwald are all at mole fractions of dioxane of less than 0.33. They give  $GE$  about 3 % larger than that of Vierk.

The heat of mixing measured by Vierk at 20° C (fig. 8) has been confirmed by the three new measurements at 25° C reported below. The excess heat capacity of the system has been calculated from the measurements of Stallard and Amis and is shown in fig. 9.

The densities of Hovorka and of Griffiths at 25° C agree and lead to the excess volume shown in fig. 10. Griffiths' measurements will not support the impossible discontinuities which he has reported in the partial molar volume at mole fractions of dioxane between 0.4 and 0.8.

FIG. 8.—Excess free-energy and enthalpy as a function of mole fraction of dioxane.

Curve 1,  $G^E$  from Vierk<sup>9</sup> (25° C);

curve 2,  $G^E$  from Bacarella, Finch and Grunwald<sup>10</sup> (25° C);

curve 3,  $H^E$  from Vierk<sup>9</sup> (20°) circles, and present measurements (25° C) triangles.

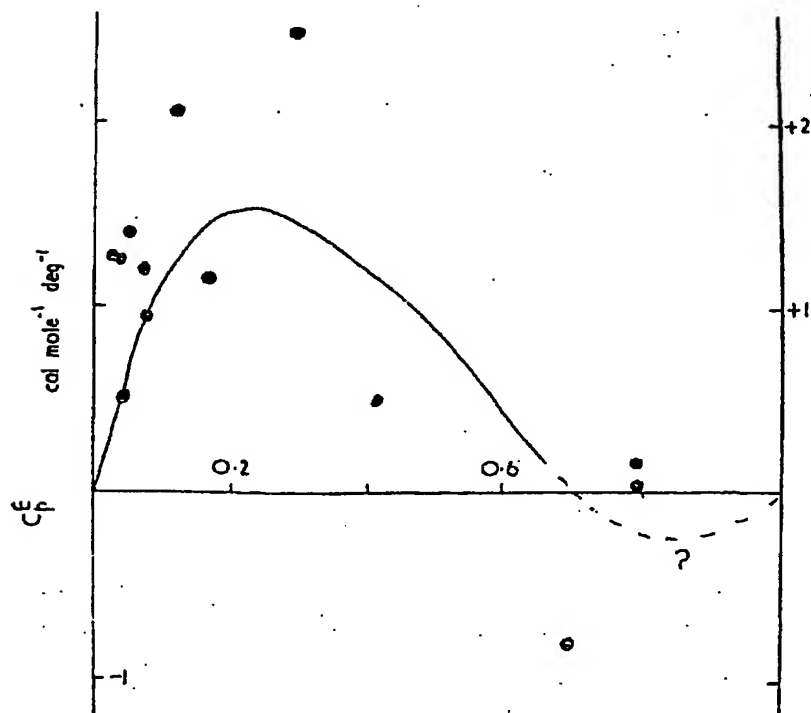
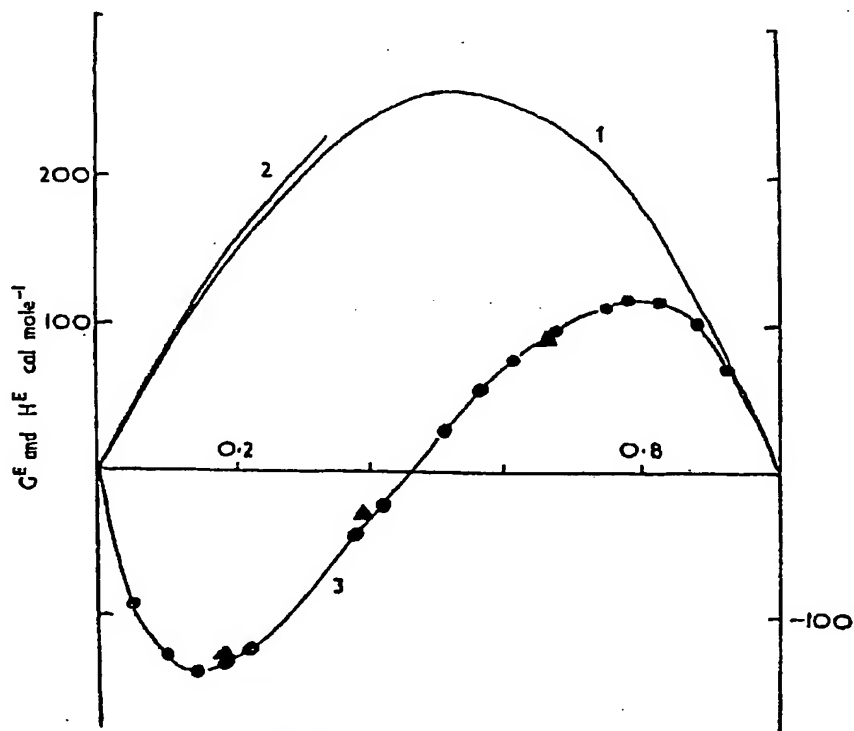


FIG. 9.—Excess heat capacity at 40° C as a function of the mole fraction of dioxane, from Stallard and Amis.<sup>11</sup>

PRESENT MEASUREMENTS.—A.R. dioxane was fractionally distilled and refluxed with liquid sodium. The dioxane was shown to be completely dry and free from all substances containing active hydrogen by the immediate formation of a coloured complex on adding a little fluorenone.<sup>13</sup> The dioxane, containing a small amount of complex in solution, was stored *in vacuo*. Mixtures were made up by weight by distillation of the de-gassed components into evacuated tubes fitted with glass break-seals.



The vapour pressures were measured by observing on a mercury manometer the pressure differences between the mixtures and pure water. Tubes containing the mixture and the water were heated in a vapour thermostat. The vapour pressures of water were those recommended by Dorsey.<sup>2</sup>

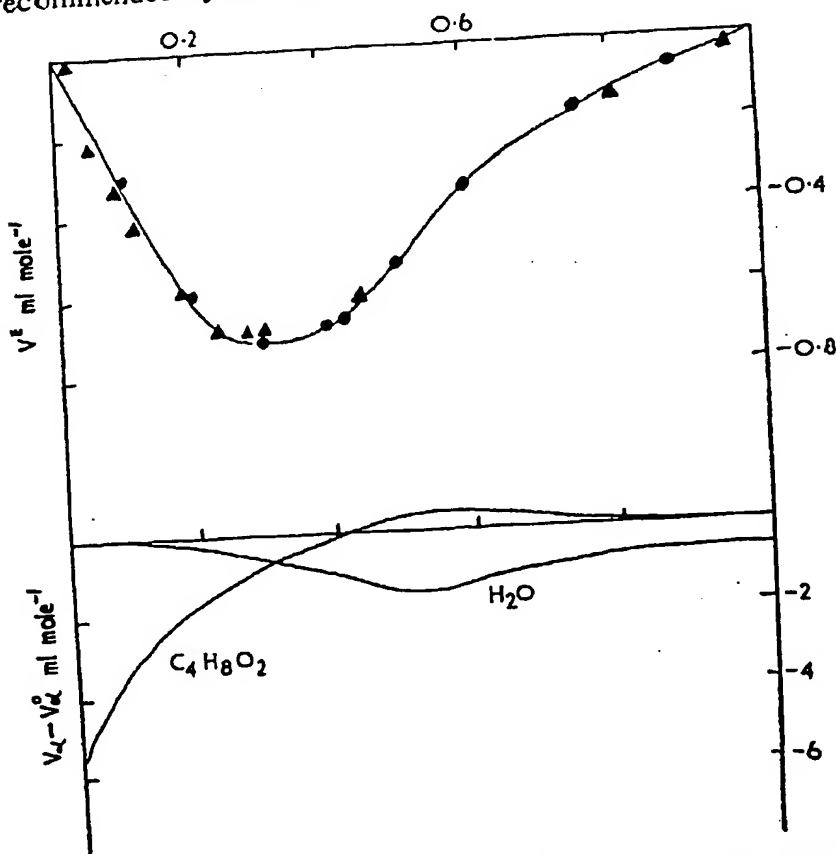


FIG. 10.—Excess volume at 25° C as a function of the mole fraction of dioxane, from Hovorka, Schaeffer and Dreisbach<sup>8</sup> (circles), and from Griffiths (triangles). Partial molar volumes from the curve for  $V^E$ .

The heats of mixing were measured in a U-tube calorimeter which has been described previously.<sup>14</sup>

TABLE 4.—VAPOUR PRESSURES IN mm Hg

mole fraction dioxane	0.000	0.260	0.535	0.760	0.820	1.000
temp. °C						
100	760	1138	1151	1110	1077	733
110	1075	1571	1581	1496	1462	986
120	1489	2130	2135	2001	1953	1304
130	2026	2837	2833	2628	2556	1696
140	2711	3722	3703	3390	3265	2174
150	3571	4808	4763	4300	4181	2752
156	4184	5556	5517	4927	4785	3156

The vapour pressure of pure dioxane can be approximately represented by

$$\log_{10} p \text{ (mm Hg)} = 7.72713 - 1813.98/(t^\circ \text{C} + 273.16)$$

with a maximum relative error (at 100° C) of 0.4 %. The observed boiling point was 101.2° C. These results agree with the measurements of Højendahl<sup>15</sup> within the error of  $\pm 2$  % which he assigns to his results.

TABLE 5.—HEATS OF MIXING AT 25° C

mole fraction dioxane	0.175	0.388	0.601
$\Delta H$ (cal mole <sup>-1</sup> )	-130.5	-30.4	+70.2

Three mixtures of mole fraction of dioxane of 0.18, 0.39 and 0.60 were heated in evacuated sealed tubes to 240° C in a bath of glycerol. Neither opalescence nor the separation of a second liquid phase was observed.

## DISCUSSION

This system comes close to satisfying the conditions for a lower consolute point over the whole temperature range from 25 to 156° C. The excess free energy at 25° C is shown in fig. 8, and two estimates of that at 150° C in fig. 11. One of these estimates is based on the observed vapour pressures but with no correction for the deviations from the perfect gas laws. These deviations will be large but their relative effect on  $GE$  is probably not

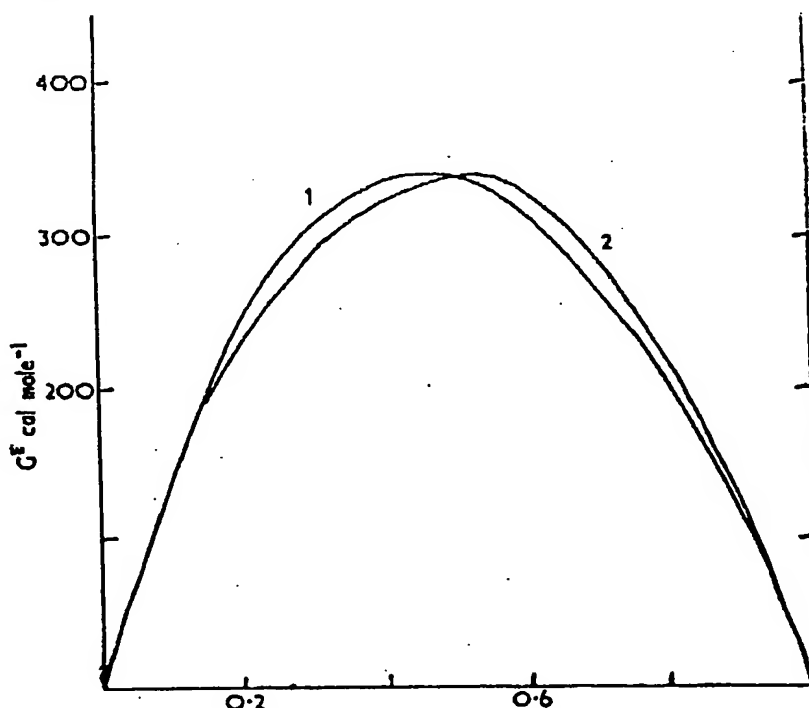


FIG. 11.—Estimates of  $GE$  at 150° C from (1) vapour pressures at 150° C and (2) from  $HE$ ,  $SE$  and  $C_pE$  at lower temperatures (see text).

serious owing to its unusually large size. The second estimate is a calculation from  $HE$  and  $TSE$  at 25° C and  $C_pE$  at 40° C with the additional assumption that  $C_pE$  is independent of temperature. The agreement between the two estimates is remarkably good. It is found that  $GE$  is about 10 % too small for curves of these shapes, at both 25 and 150° C for the system to show a consolute point. This is in agreement with direct observation. The nearness of the system to phase separation is shown by the readiness with which this occurs in the presence of an electrolyte. For example, as little as 0.005 (mole fraction) of HCl causes phase separation at room temperature.<sup>16</sup>

A comparison of the properties of this system with solutions of polyethylene glycols is made in the body of this paper.

- <sup>1</sup> Taylor and Rowlinson, *Trans. Faraday Soc.*, 1955, 51, 1183.
- <sup>2</sup> Dorsey, *Properties of Ordinary Water Substance* (Reinhold, N.Y., 1940).
- <sup>3</sup> Beynon and Humphries, *Trans. Faraday Soc.*, 1955, 51, 1065.
- <sup>4</sup> Coffin, Devins, Dingle, Greenblatt, Ingraham and Schrage, *Can. J. Res. B*, 1950, 28, 579.
- <sup>5</sup> Baughan, Jones and Stewart, *Proc. Roy. Soc. A*, 1954, 225, 478.
- <sup>6</sup> Gee, *Quart. Rev.*, 1947, 1, 282. Fricke and Lüke, *Z. Elektrochem.*, 1930, 36, 309.
- <sup>7</sup> Prigogine and Defay, *Chemical Thermodynamics* (Longmans, London, 1954), p. 431.
- <sup>8</sup> Hovorka, Schaeffer and Dreisbach, *J. Amer. Chem. Soc.*, 1936, 58, 2264.
- <sup>9</sup> Vierk, *Z. anorg. Chem.*, 1950, 261, 283.
- <sup>10</sup> Bacarella, Finch and Grunwald, *J. Physic. Chem.*, 1956, 60, 573.
- <sup>11</sup> Stallard and Amis, *J. Amer. Chem. Soc.*, 1952, 74, 1781.
- <sup>12</sup> Griffiths, *J. Chem. Soc.*, 1952, 1326; 1954, 860.
- <sup>13</sup> Morantz and Warhurst, *Trans. Faraday Soc.*, 1955, 51, 1375.
- <sup>14</sup> Thacker and Rowlinson, *Trans. Faraday Soc.*, 1954, 50, 1036.
- <sup>15</sup> Højendahl, *Danske Vid. Selsk. Mat.-Fys. Medd.*, 1946, 24, no. 2.
- <sup>16</sup> Robinson and Selkirk, *J. Chem. Soc.*, 1948, 1460.

## Polypropylene Glycols (PPGs)

### Overview

Polypropylene glycols are polymers of propylene oxide. They are clear, viscous liquids with low pour points. Viscosity increases and water solubility decreases with increasing molecular weight.

PPGs can be blended to obtain liquids with intermediate viscosities. The molecular weights range from low for water-soluble to high for water-insoluble applications.

### Properties

Series	INCI/CTFA Nomenclature	Average Molecular Weight	Specific Gravity <sup>(1)</sup>	Average Viscosity <sup>(2)</sup>			Flash Point <sup>(3)</sup>	Average Pour Point <sup>(4)</sup>	Cloud Point <sup>(5)</sup>		Refractive Index <sup>(7)</sup>
				25°C	40°C	100°C			1% aqueous	10% solvent <sup>(6)</sup>	
Units			25/25°C	cSt	cSt	cSt	°C	°C	°C	°C	@25°C
P400E	PPG-12	425	1.007	68	31	5	>150	-49	>95	69	1.445
P600E	PPG-15	600	1.003	84	38	6	227	-47	65	57	1.4465
P1000E	PPG-17	1000	1.003	143	71	11	>150	-43	21	38	1.447
P1200E	PPG-20	1200	1.003	160	80	13	174	-41	20	32	1.448
P2000E	PPG-26	2000	1.002	230	143	24	198	-31	15	20	1.449
P4000E	PPG-34	4000	1.004	1110	438	73	185	-20	9	10	1.450

#### Test Methods:

<sup>1</sup> Specific Gravity: ASTM D 892

<sup>2</sup> Viscosity: ASTM D 445

<sup>3</sup> Flash Point: ASTM D 92

<sup>4</sup> Pour Point: ASTM D 97

<sup>5</sup> Cloud Points: ASTM D 2024

<sup>6</sup> 10% surfactant in a solution of 25% Diethylene glycol butyl ether in water.

<sup>7</sup> Refractive Index: ASTM D 1218

### Details

For additional information regarding any DOW products, please contact your local distributor.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**